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14. ABSTRACT During this program, we have worked to develop a fundamental understanding of the chemical and tribological issues related to the implementation of layered solid lubricants in aerospace mechanisms. The work has entailed chemical studies performed from a surface analytical approach, tribological measurements performed over a range of length scales, and the correlation of the two classes of information. Research activities have focused on the properties of single crystal MoS ₂ and PbS and the implementation of a UHV tribometer being used to explore the properties of MoS ₂ containing composite films.					
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Final Report

Air Force Grant # FA9550-08-1-0027

Fundamentals of Solid Lubrication

For the period: 01/01/2008-11/31/2011

Contract initiation date: 01/01/08

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2. Objectives:

The *goal* of the funded research plan was to develop a fundamental understanding of the atomic-scale mechanisms by which solid lubricant systems successfully operate and the chemical and physical events responsible for their observed environmentally dependent performance. In order to achieve this goal, the following *objectives* were pursued:

- Characterize the surface chemical activity of model single crystal samples of sulfur-based solid lubricants with respect to adsorption site, reaction products, reaction cross section, and temperature.
- Measure the fundamental (absence of wear) shear strength of model solid lubricant interfaces on a nanometer scale (single grain), under controlled/vacuum environments, and as a function of tribopair composition and elevated surface temperatures.
- Design/implement a vacuum tribometer to allow correlated measurements of surface composition and environmentally specific tribological performance of thin film solid lubricants.
- Correlate shear strengths measured across length scales and pressure ranges in order to identify microscopic mechanisms contributing to macroscopic sliding and wear behavior.

3. Status of Field:

Despite a number of successful applications, the mechanisms by which low friction can be sustained at interfaces involving solid lubricants is poorly understood. The general state of understanding has been restricted by the complex nature of the sliding/buried interface, the presence and often-simultaneous participation of multiple materials, and the extreme operating conditions for which solid lubricants are intended. The variability of environment in which such materials are developed and ultimately operated also contributes to the complexity of solid lubricants. A fundamental understanding of the chemical and physical properties contributing to the performance of solid lubricants is required in shaping the future development of solid lubricant systems possessing the enhanced tribological performance required of DOD applications. During this program, we worked to develop a fundamental understanding of the chemical and tribological issues related to the implementation of layered solid lubricants in aerospace mechanisms. The work entailed chemical studies performed from a surface analytical approach, tribological measurements performed over a range of length scales, and the correlation of the two classes of information. The findings of this effort are highlighted in the following section.

4. Programmatic Findings

First-principles determination of static potential energy surfaces for atomic friction in MoS₂ and MoO₃.

Using first-principles electronic-structure calculations of static potential energy surfaces, we investigated the atomic-scale energetic barriers encountered during sliding at MoS₂ (001) and MoO₃ (001) surfaces and at the MoS₂/MoO₃ interface. The results indicate the minimum energy path to sliding and provide an upper bound to the force that must be applied in order to initiate

sliding. The results further suggest that the lowest energy pathway is to slide MoO_3 over MoS_2 along the channel direction formed by S atoms at the sliding interface, and the highest energy pathway involves MoO_3 (001) interlayer sliding, which is consistent with the results of experimental microscopic investigations of similar crystalline interfaces.

Transition from Thermal to Athermal Friction under Cryogenic Conditions.

Atomic scale frictional forces encountered as a function of temperature for the contact of a Si_3N_4 probe tip and the basal plane of MoS_2 have been measured with atomic force microscopy over the temperature range 100-500 K. Friction is observed to increase exponentially with decreasing temperature from 500 to 220 K. An Arrhenius analysis of the temperature dependent friction over this range yields an effective activation energy of ~ 0.3 eV for the thermally activated stick-slip motion of the probe tip on this surface. As temperature is reduced further below 220 K, a distinct transition to a largely athermal behavior is detected and is shown to result from the onset of interfacial wear, entailing an alternative energy dissipation pathway.

A Possible Link Between Macroscopic Wear and Temperature Dependent Friction Behaviors of MoS_2 Coatings

Studies to explore the nature of friction, and in particular thermally activated friction in macroscopic tribology, have lead to a series of experiments on thin coatings of molybdenum disulfide. Coatings of predominantly molybdenum disulfide were selected for these experiments; five different coatings were used: MoS_2/Ni , MoS_2/Ti , $\text{MoS}_2/\text{Sb}_2\text{O}_3$, $\text{MoS}_2/\text{C}/\text{Sb}_2\text{O}_3$, and $\text{MoS}_2/\text{Au}/\text{Sb}_2\text{O}_3$. The temperatures were varied over a range from -80°C to 180°C . The friction coefficients tended to increase with decreasing temperature. Activation energies were estimated to be between 2 and 10 kJ/mol from data fitting with an Arrhenius function. Subsequent room temperature wear rate measurements of these films under dry nitrogen conditions at ambient temperature demonstrated that the steady-state wear behavior of these coatings varied dramatically over a range of $K = 7.9 \times 10^{-6}$ to $2.9 \times 10^{-8} \text{ mm}^3/(\text{Nm})$. It was further shown that an inverse relationship between wear rate and the sensitivity of friction coefficient with temperature exists. The highest wear-rate coatings showed nearly athermal friction behavior, while the most wear resistant coatings showed thermally activated behavior. It is hypothesized that athermal behavior is characteristic of systems experiencing gross wear. In macroscopic tribology, thermally activated behavior is reserved for systems with stable interfaces and ultra-low wear.

Temperature-Dependent Atomic Scale Friction and Wear on $\text{PbS}(100)$

AFM measurements have documented the temperature dependent nature of friction measured on atomically flat $\text{PbS}(100)$ surfaces and the role of interfacial wear in altering the exponential increase in friction with decreasing temperatures. At room temperature and above, the $\text{PbS}(100)$ surface exhibited low friction ($\mu < 0.05$) in contact with a silicon nitride probe tip, which in the absence of wear, increased exponentially with decreasing temperature. Upon reaching a threshold value of interfacial friction near 200 K, the interaction transitioned to an athermal behavior associated with the onset of interfacial wear. In general, atomic scale wear was observed to strongly depend on the local contact pressure, to occur through layer-by-layer removal, and to correlate with higher interfacial friction. The nature of these results portray the

intricate pathways of material interaction and deformation at sliding interfaces and highlight the potential for characterizing such process at the atomic scale.

The Role of Water in Modifying Friction within MoS₂ Sliding Interfaces

Friction on single-crystal MoS₂ has been investigated with AFM as a function of relative humidity, using both a bare Si₃N₄ tip and a MoS₂-coated tip. In both cases, the friction shows an increase with increasing relative humidity. For the bare Si₃N₄ tip, a modest increase is observed in the absence of changes in interfacial adhesion or the occurrence of interfacial wear. For the MoS₂-coated tip, a sharp rise in friction is detected near 50% RH and is accompanied by an increase in adhesion and the onset of wear. Through comparisons to results obtained on HOPG using identical probe tips where little evidence of an environmental dependence is found, water is seen to have a high affinity for bridging between two MoS₂ planes, in turn drastically altering the tribological properties of this material at higher humidities. As with previous studies, the results presented here suggest that caution should be exercised when employing solid lubricants containing MoS₂ in applications involving exposure to water vapor. Under such conditions, such lubricants can be anticipated to exhibit an increase in both friction and wear, significantly limiting the tribological performance of the application.

Environmental Effects on the Tribology and Microstructure of MoS₂-Sb₂O₃-C Films

The tribology of MoS₂-Sb₂O₃-C films was tested under a variety of environmental conditions (ambient 50% RH, 10⁻⁷ Torr vacuum, 150 Torr oxygen, and 8 Torr water) and correlated with the composition of the surface composition expressed while sliding. High friction and low friction modes of behavior were detected. The lowest coefficient of friction, 0.06, was achieved under vacuum, while sliding in 8 Torr water and ambient conditions both yielded the highest value of 0.15. Water vapor was determined to be the environmental species responsible for high friction performance. XPS evaluations revealed a preferential expression of MoS₂ at the surface of wear tracks produced under vacuum and an increase in Sb₂O₃ concentration in wear tracks produced in ambient air (50% RH). In addition, wear tracks produced by sliding in vacuum exhibited the lowest surface roughness as compared to those produced in other environments, consistent with the picture of low friction originating from well-ordered MoS₂ layers produced through sliding in vacuum.

Water Intercalation between MoS₂ Layers Produces an Increase in Interfacial Shear Strength

The friction of discrete, atomically thin molybdenum disulfide (MoS₂) islands/flakes supported on MoS₂ single crystal substrates has been investigated at low (~10%) and high (~90%) relative humidities, with atomic force microscopy (AFM). MoS₂ flakes were generated through the exfoliation of lithium intercalated MoS₂ in water. A drop of water solution containing suspended MoS₂ flakes was placed on a MoS₂ single crystal surface with a syringe and allowed to evaporate, leaving behind isolated MoS₂ islands. The frictional properties of the interface formed between the MoS₂ flake and the MoS₂ substrate was investigated by employing an AFM tip to push the flake across the surface, recording the lateral force required to initiate sliding. The friction forces were measured over a series of MoS₂ thin flakes with sizes ranging from 0.002 to

0.21 μm^2 . From these measurements, shear stresses of 0.34 ± 0.02 MPa for sliding in a 10% RH environment and 0.69 ± 0.02 MPa for 90% RH were determined,. The result indicates that the frictional properties of MoS₂ are heavily influenced by the presence of molecular water *between* MoS₂ layers.

5. Personnel Supported

Kevin Chaput, Veronic Boesen, Michael Brady, Joelle Payne, undergraduate research (hourly)
Ted Limpoco, graduate student, 50%
Greg Dudder, graduate student, 50%
Kevin Gilley, graduate student, 50%
Xueying Zhao, Postdoctoral Fellow, 100%
Dr. Scott S. Perry, Professor, 8.3% (1 month summer)

6. Publications and Presentations

Liang, Tao; Sawyer, W. Gregory; Perry, Scott S.; Sinnott, Susan B.; Phillpot, Simon R. *First-principles determination of static potential energy surfaces for atomic friction in MoS₂ and MoO₃*. Physical Review B: Condensed Matter and Materials Physics (2008), 77(10), 104105/1-104105/6.

Zhao, Xueying; Phillpot, Simon R.; Sawyer, W. Gregory; Sinnott, Susan B.; Perry, Scott S.. **Transition from Thermal to Athermal Friction under Cryogenic Conditions.** Physical Review Letters (2009), 102(18), 186102/1-186102/4.

Hamilton, Matthew A.; Alvarez, Luis A.; Mauntler, Nathan A.; Argibay, Nicolas; Colbert, Rachel; Burris, David L.; Muratore, Chris; Voevodin, Andrey A.; Perry, Scott S.; Sawyer, W. Gregory. **A Possible Link Between Macroscopic Wear and Temperature Dependent Friction Behaviors of MoS₂ Coatings.** Tribology Letters (2008), 32(2), 91-98.

Author(s): Zhao, XY (Zhao, Xueying); Phillpot, SR (Phillpot, Simon R.); Sawyer, WG (Sawyer, W. Gregory); Sinnott, SB (Sinnott, Susan B.); Perry, SS (Perry, Scott S.)
Title: Comment on "Transition from Thermal to Athermal Friction under Cryogenic Conditions" Reply
Source: PHYSICAL REVIEW LETTERS, 105 (22): Art. No. 229602 NOV 23 2010

Author(s): Zhao, XY (Zhao, Xueying); Perry, SS (Perry, Scott S.)
Title: Temperature-Dependent Atomic Scale Friction and Wear on PbS(100)
Source: TRIBOLOGY LETTERS, 39 (2): 169-175 AUG 2010

Author(s): Zhao, XY (Zhao, Xueying); Perry, SS (Perry, Scott S.)
Title: The Role of Water in Modifying Friction within MoS₂ Sliding Interfaces
Source: ACS APPLIED MATERIALS & INTERFACES, 2 (5): 1444-1448 MAY 2010

Gregory J. Dudder · Xueying Zhao · Brandon Krick · W. Gregory Sawyer · Scott S. Perry

7. Interactions/Transitions

The use of solid lubricant components in spacecraft mechanisms is presently practiced throughout the industry. In general, our contact and collaboration with Aerospace Corporation will continue to provide opportunities to transmit the information directly to contractors involved in the manufacture of space hardware, leading to improved performance of Air Force, DoD, and NASA space systems.

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8. New discoveries, inventions, or patent disclosures.

9. Honors/Awards:

Prof. Scott S. Perry
2008 Chair Gordon Research Conference "Chemistry at Interfaces"

Prof. Scott S. Perry
2007-2008 Department of Materials Science and Engineering Faculty Excellence Award
University of Florida

Prof. Scott S. Perry
2008-2009 Department of Materials Science and Engineering Faculty Excellence Award
University of Florida

Prof. Scott S. Perry
2009-2010 Department of Materials Science and Engineering Faculty Excellence Award
University of Florida

Other Programmatic Information

Changes in research objectives, if any: None

Change in AFOSR program manager, if any: Position presently vacant.

Extensions granted or milestones slipped, if any: 1 year no-cost extension granted.